

# ON THE “SIX ORDERS OF MAGNITUDE” DIFFERENCE IN THE FRAGMENTATION KINETIC RATE CONSTANT IN RAFT POLYMERIZATION

Gabriel Jaramillo-Soto, Jhonatan Pallares and Eduardo Vivaldo-Lima\*

*Universidad Nacional Autónoma de México (UNAM), Facultad de Química, Departamento de Ing. Química, Conjunto E, CP 04510, México D.F., México. [vivaldo@servidor.unam.mx](mailto:vivaldo@servidor.unam.mx)*

**Abstract** - Using a detailed mathematical model for RAFT polymerization recently reported in the literature (1), it is demonstrated that the controversy in the literature regarding the “six orders of magnitude difference” in the fragmentation rate coefficient, and the “concern” about the “validity” of the commercial software package Predici® to represent the RAFT mechanism have nothing to do with model inadequacy or the alluded “empirical nature” of Predici®. Rather, these issues are merely a matter of not having precise parameter estimates in a very complex, multi-parameter model, where similar model profiles can be generated with different combinations of model parameters.

## Introduction

There is an ongoing controversial debate in the literature regarding the mechanism that causes rate retardation phenomena in some RAFT polymerization systems (see for instance the corresponding section of reference 2). The analysis of this problem has created another debate about the magnitude of the fragmentation rate constant ( $k_b$  in our nomenclature) for some of these RAFT polymerization systems. Wang and Zhu (3) used a value of  $k_b=10^4 \text{ s}^{-1}$  in the reference set of kinetic rate constants for their model simulations, and suggested in their conclusions that the radical adduct (the macroRAFT radical) was a very short-lived species. Barner-Kowollik et al. (4) criticized that statement from Wang and Zhu (3) and pointed out that there is experimental and theoretical evidence suggesting that the macroRAFT radical is a stable species with a lifetime longer than the 0.0001 s assumed by Wang and Zhu (3). They also pointed out that Wang and Zhu (3) used a very high value of the cross-termination kinetic rate constant, and that they provided a purely simulation study, with no experimental data. In replying to the comments from Barner-Kowollik et al. (4), Wang et al. (5) provided an explanation of how the kinetic rate constants were chosen, and addressed other related issues. However, in their reply paper, Wang et al. (5) criticized the “amended” scheme used by Barner-Kowollik et al. (6) to simulate the RAFT process with the Predici® software, stating that the concentration of the macroRAFT radicals could not be calculated with that scheme, and regarded the Predici® modeling of RAFT as semiempirical. Wulkow et al. (7) subsequently described the mathematical model behind the Predici® implementation from Barner-Kowollik et al. (6) of the RAFT process, and concluded that the implementation using two memory distribution species is a valid and quantitative translation of the original CSIRO-suggested RAFT mechanism (2,8). Unfortunately, they did not provide calculations of the concentration profiles of the macroRAFT radicals, which was one of the aspects criticized by Wang et al. (5).

In this contribution we present a comprehensive mathematical model for the RAFT process, based on a detailed reaction mechanism. Molecular weight development is calculated using the method of moments. The resulting mathematical model is similar to the one proposed by Zhang and Ray (9), but our model includes the possible termination reaction between macroRAFT radicals and living polymer radicals (10-13), and thermal self-initiation, both cases not considered by Zhang and Ray (9). Our model can easily reduce to simpler reaction mechanisms proposed by others, by adequate selection of the initial conditions and the values of some of the kinetic rate constants. Three different reaction mechanisms used in the literature are compared, and the validity of the predictions

obtained with the Predici® commercial software is also addressed. The “typical” polymerization conditions used by Wang and Zhu (3) in their simulations and the RAFT polymerization of styrene using cumyl dithiobenzoate and 2,2-azobisisobutyronitrile (AIBN) at 60 °C (6) were used as reference cases for our modeling study.

## Modeling

The mathematical model used in this contribution has been described in detail by Pallares et al. (1). The complete model (Model 1) of reference 1 consists of 46 simultaneous ordinary differential equations (ODEs), 15 for small molecules (equations 1 to 15 in reference 1), and 31 moment equations. The model equations were implemented in a Fortran computing program. Subroutine DDASSL (14) was used to numerically integrate the ODEs. The simulations presented in this study were generated using this code. Most of them were reproduced using the Predici® commercial software.

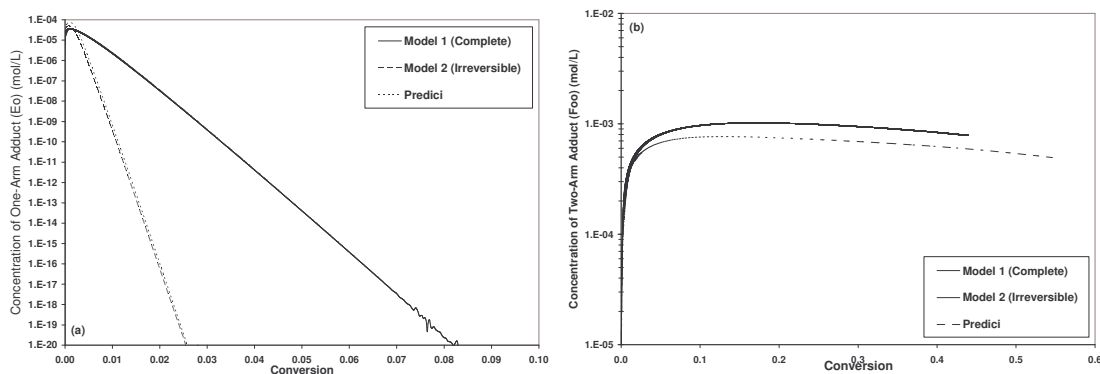
## Results and Discussion

Figure 1 shows predicted profiles of concentrations of one- (Figure 1a) and two-arm (Figure 1b) polymer adduct ( $E_0$  and  $F_{00}$ , respectively) versus monomer conversion, at the polymerization conditions of Case 2 of reference 1. It is observed that the one-arm adduct is consumed very rapidly, starting from a fairly large concentration, in the order of  $10^{-5}$  mol L<sup>-1</sup>, to an almost complete depletion. By the time 10% of the monomer is consumed, there is practically no one-arm adduct left in the system. In the case of the two-arm polymeric adduct, there is an even larger concentration (close to 0.001 mol L<sup>-1</sup>) and although it decreases with time, it does so rather slowly (see Figure 1b). One interesting aspect to point out is that the Predici® simulations and the Fortran simulations with Model 2 of reference 1 for the case of  $E_0$  (Figure 1a) agree very well.  $E_0$  in Predici® was obtained directly from the concentration of variable “RMAB(s)” (see Table 3 of reference 1) and  $F_{00}$  was obtained from the concentration of the “memory” variable used in Predici® to account for the adduct (either D(s) or DA(s) from Table 3 of reference 1). The predicted profile of  $E_0$  versus time with Model 1 decays less rapidly but still the agreement is good. In the case of  $F_{00}$ , Models 1 and 2 overlap, and the Predici® profile deviates a little, but the agreement is still satisfactory. These results show two important aspects: (1) at the conditions of Case 2 the one-arm adduct is a short lived species, but the two-arm adduct is rather stable, and (2) the predictions of  $E_0$  and  $F_{00}$  obtained with Predici® agree very well with the results obtained with the model of Wang and Zhu (3) (Model 2 of this paper). We will revisit these statements shortly.

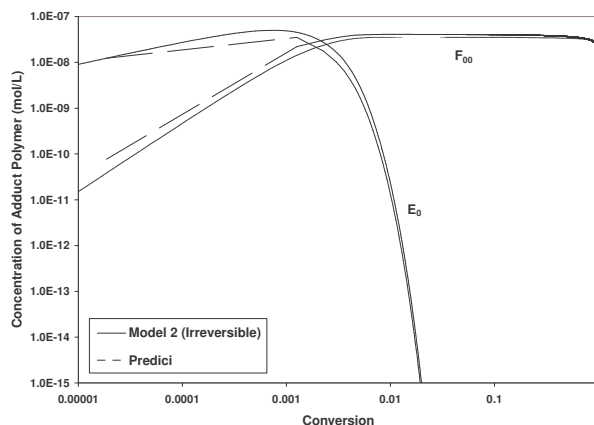
It is observed in Figure 2 that the agreement between Model 2 and Predici® is very good, namely, we can calculate without any problem the concentration profiles of the adduct polymeric species using Predici®. Another interesting observation is that at the conditions of Case 1 the maximum concentration of  $E_0$  is much lower than in case 2 and also decreases very rapidly, whereas  $F_{00}$  again decreases more slowly and its concentration is very low, an indication that these radicals are short-lived species (meaning that as soon as they are produced they are consumed).

The results obtained for case 2 (see 1 and 2 above) suggest that Barner-Kowollik et al. (4) are correct when they state that the polymer adduct is a stable species. However, the results obtained for Case 1 (see reference 1) indicate that Wang and Zhu (3) are also correct when they state that the polymeric adduct is a short-lived species. In other words, the polymer adduct is stable when  $k_b = 10^{-2}$  s<sup>-1</sup> and it is a short-lived species when  $k_b = 10^4$  s<sup>-1</sup>. What is the true physical nature of these radical species needs to be further studied, but what is

clear is that the models which consider the presence of the adduct (Models 1 and 2 of this paper), this last one being the same as the model by Wang and Zhu (3)) can capture well these possible operating regions. These results show the necessity of finding more direct ways to estimate some of the kinetic rate constants associated to complex reaction mechanisms, such as the RAFT one. Another important aspect to point out is that Wang et al. (5) are incorrect when they state that the concentrations of the polymeric adducts can not be calculated with Predici®.



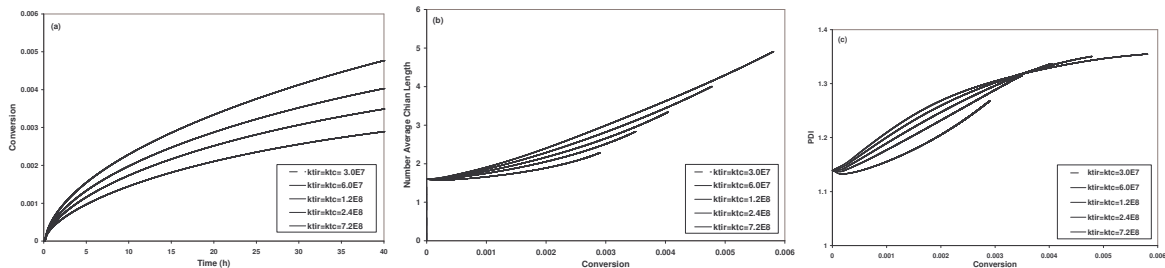
**Figure 1.** Comparison of model predictions for (a) concentration of one-arm adduct ( $E_0$ ) versus conversion, and (b) concentration of two-arm adduct ( $F_{00}$ ) versus conversion, obtained with the Fortran implementation of models 1 and 2, and the Predici® implementation of Model 2, for the RAFT polymerization of styrene with cumyl dithiobenzoate and AIBN at 60 °C. Polymerization conditions and kinetic parameters as in Figure 7 of reference 1.



**Figure 2.** Evolution of the concentration profiles of one-arm ( $E_0$ ) and two-arm ( $F_{00}$ ) polymer adduct molecules, at the polymerization conditions and with the kinetic parameters listed in the caption of Figure 2 of reference 1.

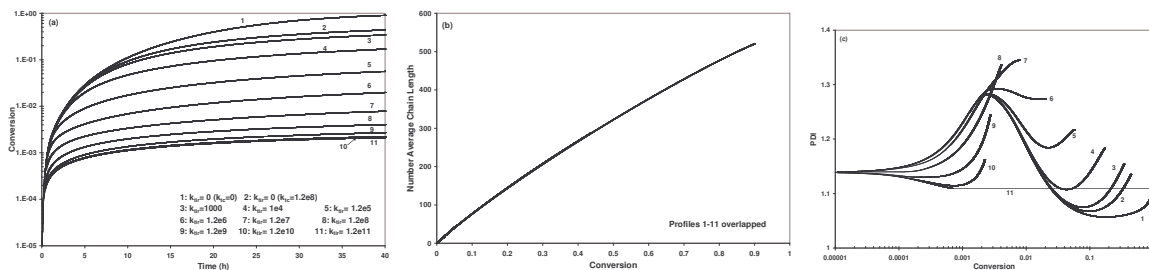
Figures 3 and 4 show the importance of the magnitude of the rate of formation of three-arm dead polymer (intermediate termination) from the reaction between two-arm polymeric adduct and linear polymer radical molecules, represented by the magnitude of the kinetic rate constant  $k_{tir}$ , on polymerization rate and molecular weight development of the RAFT polymerization of styrene at 60 °C using cumyl dithiobenzoate and AIBN (Case 2). In the simulations of Figure 3 it is assumed that  $k_{tc} = k_{tir}$ , so that both constants are varied together. In Figure 4  $k_{tc}$  is assumed independent of  $k_{tir}$ .

It is observed in Figure 3a that if  $k_{tc}$  takes on the typical values of termination by combination in conventional free-radical polymerization (which seems adequate for CLRP), the polymerization proceeds extremely slowly. This strong retardation effect does not seem to significantly affect the number average molecular weight in the early stages of the polymerization (Figure 3b), and it seems to only affect the PDI values at extremely low conversions (Figure 3c). Although the formation of three-arm stars seems like a plausible explanation of the retardation effect, it seems from our simulations that the kinetic rate constant associated to that reaction ( $k_{tir}$ ) should be much lower than  $k_{tc}$  (a chemically-controlled  $k_t$  in general).



**Figure 3.** Effect of the kinetic rate constant for formation of three-arm polymer ( $k_{tir}$ ) on (a) polymerization rate (conversion versus time), (b) number average molecular weight versus conversion, and (c) PDI versus conversion, assuming  $k_{tir} = k_{tc}$ .

The case of  $k_{tir} \leq k_{tc}$ , shown in Figure 4, seems more likely. It is observed that the polymerization rate can be easily tuned to any observed experimental data by adequately choosing the value of  $k_{tir}$  (see profiles 2 to 11 in Figure 4a), without significantly affecting the  $\overline{rn}$  versus conversion profile, as observed in Figure 4b, and with only significant effects on PDI in the very early stages (low conversions) of the polymerization (Figure 4c). It has been established that the retardation effect is not a one factor problem, depending on the particular RAFT agent/monomer combination, and the polymerization conditions. In this section we only addressed the specific explanation based on the formation of a three-arm dead polymer molecule, put forward in references (10-13). The models proposed (or evaluated) here can also be used as a valuable tool to address these (and other) issues.



**Figure 4.** Effect of the kinetic rate constant for formation of three-arm polymer ( $k_{tir}$ ) on (a) polymerization rate (conversion versus time), (b) number average chain length versus conversion, and (c) PDI versus conversion.

## Concluding Remarks

It was demonstrated that the literature controversy around the six order of magnitude difference in the value of  $k_b$  has nothing to do with inadequate modeling. It is only related to the specific values of the kinetic rate constants chosen, which can represent equally plausible yet very different physical situations. Modeling and experimentation complement each other, and both may be heavily influenced by the appropriate design of experiments and effective parameter estimation (especially with highly correlated parameters in kinetic models). In many situations in polymerization modeling, especially with new systems like RAFT, not only availability but also reliability of process data may accentuate the importance of the above issues (and are usually the cause of many misinterpretations). Also, we have shown herein that the Predici® implementation of the RAFT process is correct (in agreement with Wulkow et al. (7)), and have explicitly demonstrated this via calculations of the concentrations of one- and two-arm adduct species.

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